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PROPERTIES OF MISCIBLE POLYMER BLENDS(U) TEXAS UNIV AT
AUSTIN DEPT OF CHEMICAL ENGINEERING D R PAUL ET AL.
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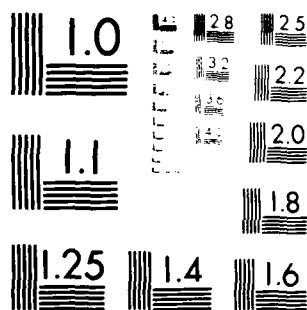
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The physical properties of a variety of miscible and partially miscible binary polymer blends were evaluated. Where possible, these properties were related to the intermolecular interactions responsible for blend miscibility. The properties of the miscible blends examined were found to be more strongly influenced by the blend composition and the inherent properties of the blend components than by the nature of the intermolecular interactions. For example, miscible polycarbonate / copolyester blends were found to thermally embrittle due to molecular relaxations when annealed for extended periods below the blend T_g; a phenomenon which is also observed for both pure components. For this same system, we have also demonstrated that the rate of hydrolysis of the polycarbonate		

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A new thermodynamic model has been developed which shows promise for understanding and predicting polymer-polymer miscibility and the "miscibility window" that is often observed when copolymers with varying monomer contents are mixed with the other blend component. Several experimental blend systems, including poly(styrene-co-maleic anhydride) / poly(styrene-co-acrylonitrile), poly(vinyl chloride) / aliphatic polyesters, Phenoxy / aliphatic polyesters, and the newly discovered poly(epichlorohydrin) blends with acrylates and methacrylates have been prepared and analyzed in terms of this model. The model suggests that miscibility may occur because the intermolecular interactions within the copolymer are unfavorable, as opposed to the more conventional view that miscibility is caused by favorable interactions between the copolymer and the other blend component.

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PROPERTIES OF MISCIBLE POLYMER BLENDS

Final Report

D.R. Paul and J.W. Barlow
September 30, 1984
U.S. Army Research Office

Grant Number: DAAG29-81-K-0147

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I. Statement of the Problem Studied

The general objectives of this work were to obtain a better understanding of the relationships between the thermodynamic interactions responsible for the formation of miscible blends and the resulting mechanical, chemical, and transport properties of the blends. A variety of binary, miscible and partially miscible blend systems, including polycarbonate/copolyester, poly(epichlorohydrin)/polyester, poly(epichlorohydrin)/polymethacrylate, poly(epichlorohydrin)/polyacrylate, poly(vinyl chloride)/polyester, poly(styrene-co-acrylonitrile) / poly(methyl methacrylate), poly(styrene-co-acrylonitrile) / poly(ethyl methacrylate), and poly(vinylidene fluoride) / poly(methyl methacrylate) were examined during the grant period. While the complete property spectra were not developed for every blend system in the above list, our work on these systems allows certain general conclusions to be made regarding miscible blend behavior. These conclusions are summarized in the following section. Details of the studies leading to these conclusions can be found in the 14 papers published during the grant period (Section III.B) and in the 7 papers submitted or accepted for publication (Section III.C)

II. Summary of Important Results

A. Thermodynamic Analysis of Blends and New Blend Systems.

The most important theme of our work has been the attempt to understand and quantify the intermolecular interactions responsible for blend miscibility and blend properties. Recently, we proposed a mathematical model to explain the observed miscibility in binary blends of a copolymer with a homopolymer (reference 12 in Section III.B of this report, hereafter referred to as III.B.12). This model suggests that copolymers may be miscible in homopolymers because the molecular interactions within the pure copolymer are unfavorable, as opposed to the more conventional view that miscibility is caused by favorable interactions between the copolymer and the homopolymer in the blend. This model successfully predicts the miscibility of SAN copolymers with SMA copolymers as functions of their acrylonitrile and maleic anhydride contents, respectively, and it suggests that the "miscibility window" observed in PVC containing and Phenoxy containing blends with aliphatic polyesters which contain varying ester carbonyl contents may also be the result of interactions within the pure components (III.B.12, III.C.5). Both the study of SAN / polyester miscible blends (III.B.5) and of miscible blends comprised of poly(epichlorohydrin)/polyester (III.B.13) serve to reinforce our developing conclusions in this area.

Work is continuing in the general area of polymer blend thermodynamics. Of particular interest, M. Fowler is examining the miscibility and LCST Behavior of SAN/PMMA and SAN/PEMA blends as a function of the AN content of the SAN copolymer. As expected, there appears to be an optimum AN content for maximum interaction with each polyester, as judged by the temperature location of the cloud point. That is, when the AN content is less than optimum, the temperature at which the blend phase separates on heating is lower. Interestingly, the optimum AN content for blends with these polyesters is somewhat less than the usual AN content available commercially. This suggests that copolymer suppliers may need to offer special compositions for specific blend applications.

Some interest has been expressed in our discovery that blends of poly(epichlorohydrin) with poly(methyl methacrylate) are miscible by U.S. Army personnel involved in rocket fuel binder systems. As a result of our interim report to ARD, J.W. Barlow of our laboratory met with Dr Porter Mitchell, U.S. Army Missile Command, Huntsville, in March, 1984, to discuss this and other blend systems as binders for rocket propellents.

B. Mechanical Properties of Miscible and Partially Miscible Blends.

During this reporting period, several publications regarding the mechanical properties of the blend comprised of polycarbonate and the copolyester KODAR A150 were issued (III.B.14, III.B.4). This system, which was discovered to be miscible and extensively studied by this laboratory during the previous grant period, is now commercially available from General Electric Company under the trade name "Xenoy-3000". This material is amorphous and tough, and it shows properties which vary in a roughly linear manner with blend composition when processed under ordinary molding conditions. However, if it is annealed for extended periods at temperatures just below the glass transition temperature, T_g , the material thermally embrittles due to simultaneous relaxations of volume and molecular orientation. It is important to note that both pure components show similar relaxations when annealed, so that the observed blend behavior should be expected. Similarly, when the blend is annealed at temperatures between the T_g and the melting temperature, T_m , of the copolyester, the copolyester will crystallize (III.B.6, III.B.14). The resulting mechanical properties of the blend at room temperature become a complicated function of blend composition, the initial state of molecular orientation, and the process history. The main effect of copolyester crystallization on the mechanical properties of the blend is to embrittle these otherwise very ductile, glassy materials.

The mechanical properties of the partially miscible blend of polycarbonate, PC, with poly(ethylene terephthalate), PET, have been evaluated (III.C.1). Although the PET is crystalline when it is added to the PC, it has a lower T_g than PC, and at PET concentrations less than 80% by weight, the crystallinity of the PET in the blend is somewhat reduced at the molding conditions usually employed. The result is that the PET serves to plasticize the PC, and blends with elongations at break which are factors of 3 to 5 times higher than those for the pure components can result. Interestingly, the moduli and yield strengths of the blends change little with composition, a situation which is probably due to the reinforcing effects of the PET crystals at high PET levels in the blend and to the already high values of these properties for PC at low PET levels in the blend.

A similar situation is seen when the mechanical properties of miscible blends containing poly(vinylidene fluoride), PVF₂, and poly(methyl methacrylate), PMMA, are examined (III.C.3). Again the crystallization of the PVF₂ from the blend is retarded at PVF₂ concentrations less than 60% by weight, and the blend properties show the increased ductility and lowered moduli and strength expected for plasticized PMMA. Beyond the 60% level, PVF₂ crystallizes more completely, and the elongation at break, or ductility, decreases sharply while the strength and moduli increase.

C. Effects of Environment on Blend Properties

The influence of humid aging on the mechanical properties of PC and its blends with KODAR A150 copolyester was examined (III.B.8). It is well known that PC has very poor hydrolytic stability and that it will rapidly show loss of molecular weight and mechanical properties in hot humid environments such as boiling water. Consequently, PC is not recommended for applications of this type. As discussed above, the copolyester also rapidly loses its ductility and becomes opaque in boiling water because it crystallizes when raised above its T_g of 88°C. It is also not recommended for boiling water applications where clarity is an issue. Interestingly, the 50/50 blend of these two materials maintains its clarity and ductility in boiling water because the higher and more stable molecular weight of the copolyester compensates for the molecular weight loss of the PC component while the higher T_g of the PC raises the blend T_g above 100 °C thereby preventing crystallization of the copolyester.

The improved molecular weight stability shown by the blend, as a result of incorporating the inherently more stable copolyester, is apparently the reason that General Electric has commercialized this material. They offer it

for applications requiring improved chemical and gamma radiation resistance.

The environmental stress crack resistance, ESCR, of poly(methyl methacrylate), PMMA, is notoriously poor, and this material will craze and crack in a variety of common chemicals, including water and alcohols. Because it is semicrystalline, the ESCR of poly(vinylidene fluoride), PVF₂, on the other hand, is excellent. A recent study of the ESCR of the miscible blend comprised of these two materials (III.C.3) shows that significant resistance to chemical stress cracking can be conferred on the PMMA component by addition of the PVF₂. The mechanism for this phenomenon seems to be largely related to the plasticization of the PMMA by the PVF₂ component, which has a lower T_g.

Recently, we have shown that plasticization of homopolymers and polymer blends can result from the sorption of carbon dioxide, CO₂, at relatively high pressures. This plasticization can induce crystallization of a semicrystalline material by the same mechanisms which are operative when liquids are dissolved in the polymers (III.C.7). The CO₂ induced crystallization of the PVF₂ component in PVF₂/PMMA blends causes the appearance of a secondary melting endotherm which varies in location from just above the T_g of the material to just below the normal PVF₂ melting point. Its location and area are seen to vary in systematic and reasonable ways as the blend composition, temperature, CO₂ pressure, and exposure time are varied. This peak evidently arises from the melting of crystals which are formed under restricted conditions and which are thus significantly smaller than those formed normally from the melt. A series of papers by J.S. Chiou of our laboratory is presently being prepared which will further discuss the effects of CO₂ sorption on the depression of blend T_g and permeation of CO₂ in this system.

D. Effect of Blend Crystallinity on Gas Permeation.

Permeation rates of Helium, Methane, and CO₂ in miscible blends of PC / copolyester were measured at 35°C. The permeabilities in blends which were thermally annealed to develop copolyester crystallinity were compared with permeabilities in fully amorphous blends. For this system, the presence of crystallinity caused a slightly greater impedance to CO₂ transport than it did with the other two gases. Of some importance to the potential application of the blend as a membrane separation device, the relative rates of permeation varied greatly with blend composition (III.B.10, III.B.3). For example, the permeation rate of Helium relative to Methane varies with blend composition from about 48 in pure PC to about 105 in the pure copolyester and is only slightly affected by copolyester

crystallinity, whereas the rate of CO_2 relative to Methane varies from 26 for pure PC to 19 for pure copolyester.

E. Continuing Studies.

Work has begun and is continuing on issues which are pertinent to our presently funded, ARO supported, research on the relationships between properties and phase behavior of multiphase immiscible blends. Three of our students are primarily involved in this activity at the present time. M. Fowler is studying the thermodynamic nature of polymer - polymer diffusion across phase boundaries by examining the rate of "re-knitting" of fractured interfaces at various temperatures below but close to T_g . M. Schwarz is developing a stress dilatometer technique which will detect the fracture at polymer - polymer interfaces, which exist in immiscible blends, when the blends are stressed in uniaxial tension. This technique should aid our understanding of the role of interfacial adhesion (and the interfacial diffusion which must be the primary cause of this adhesion) in determining blend properties. P. Tucker is presently studying the thermodynamic driving forces and other phenomena associated with the insertion of a polymer into a phase domain with which it is miscible in a multiphase system. These and other studies should lead to development of multiphase blends with improved properties.

II. Publications Completed to Date

A. Theses and Dissertations.

<u>Name</u>	<u>Title</u>
W. E. Preston (M.S.)	Mechanical and Transport Properties of Crystalline Blends of Polycarbonate and a Copolyester
S. R. Murff (M.S.)	Mechanical and Thermal Properties of Polymer Blend Systems: Poly(ethylene terephthalate)/Polycarbonate and Poly(methyl methacrylate)/Poly(vinylidene fluoride)
E. M. Woo (Ph.D.)	Structure - Miscibility Relationships for Blends Containing Polymers with Polar Functional Groups
J. S. Chiou (Ph.D., Dec. 1984)	In Preparation.

B. Papers in Print.

1. J. W. Barlow and D. R. Paul, "Polymer Blends and Alloys - Selected Considerations", Polym. Eng. Sci., 21, 985 (1981).
2. W. A. Smith, J. W. Barlow, and D. R. Paul, "Chemistry of Miscible Polycarbonate - Copolyester Blends", J. Appl. Polym. Sci., 26, 4233 (1983).
3. P. Masi, J. W. Barlow, and D. R. Paul, "Gas Sorption and Transport in a Copolyester and its Blends with Polycarbonate", J. Polym. Sci.: Polym. Phys. Ed., 20, 15 (1982).
4. E. A. Joseph, M. D. Lorenz, J. W. Barlow, and D. R. Paul, "Mechanical Properties of Miscible Polycarbonate - Copolyester Blends", Polymer, 23, 112 (1982).
5. J. S. Chiou, J. W. Barlow, and D. R. Paul, "Miscibility of SAN with Polyacrylates and Polymethacrylates", Polymer, 23, 1543 (1982).
6. R. S. Barnum, J. W. Barlow, and D. R. Paul, "Melting and Crystallization Behavior of Miscible Copolyester - Polycarbonate Blends", J. Appl. Polym. Sci., 27, 4065 (1982).

III.B (continued)

7. D. R. Paul and J. W. Barlow, "Polymer Blends: Introductory Overview and Future Developments", Ch. 1 in "Polymer Compatibility and Incompatibility: Principles and Practice", K. Solc (ed.), MMI Press Symposium Series, Vol. 2, 1982.
8. E. A. Joseph, D. R. Paul, and J. W. Barlow, "Boiling Water Aging of a Miscible Blend of Polycarbonate and a Copolyester", J. Appl. Polym. Sci., 27, 4807 (1982).
9. J. W. Barlow, D. R. Paul, and D. R. Lloyd, "Aspects of Sorption in Polymers and Polymer Blends", Proceedings of the 1983 Scientific Conference on Chemical Defense Research, Nov. 14-18, 1983 (limited circulation)
10. W. E. Preston, J. W. Barlow, and D. R. Paul, "Effect of Crystallinity on Gas Permeation in Miscible Polycarbonate - Copolyester Blends", J. Appl. Polym. Sci., 29, 845 (1984).
11. D. R. Paul, "Gas Transport in Homogeneous Multicomponent Polymers", J. Membrane Sci., 18, 75 (1984).
12. D. R. Paul and J. W. Barlow, "A Binary Interaction Model for Miscibility of Copolymers in Blends", Polymer, 25, 487 (1984).
13. A. C. Fernandes, J. W. Barlow, and D. R. Paul, "Aliphatic Polyester Miscibility with Poly(epichlorohydrin)", J. Appl. Polym. Sci., 29, 1971 (1984).
14. W. E. Preston, J. W. Barlow, and D. R. Paul, "Effect of Crystallinity on Mechanical Properties of Miscible Polycarbonate - Copolyester Blends", J. Appl. Polym. Sci., 29, 2251 (1984).

C. Papers Submitted and Accepted for Publication.

1. S. R. Murff, J. W. Barlow, and D. R. Paul, "Thermal and Mechanical Behavior of Polycarbonate - Poly(ethylene terephthalate) Blends", J. Appl. Polym. Sci.
2. J. S. Chiou, J. W. Barlow, and D. R. Paul, "Sorption and Transport of Gases in Miscible Poly(methyl acrylate) / Poly(epichlorohydrin) Blends", J. Appl. Polym. Sci.

III.C. (continued)

3. S. R. Murff, J. W. Barlow, and D.R. Paul, "Environmental Stress Cracking and Cracking of PMMA - PVF₂ Blends", Adv. Chem. Ser.
4. D. R. Paul, "Polymer Blends - Phase Behavior and Property Relationships", Adv. Chem. Ser.
5. E. M. Woo, J. W. Barlow, and D. R. Paul, "Thermodynamics of the Phase Behavior of Poly(vinyl chloride) / Aliphatic Polyester Blends", Polymer.
6. D. R. Paul, "Thermodynamic Theory and Experimental Techniques for Polymer Blends", Proceedings of NATO ASI, London, 1984.
7. J. S. Chiou, J. W. Barlow, and D. R. Paul, "Polymer Crystallization Induced by Sorption of CO₂ Gas" , submitted for publication.

IV. Participating Scientific Personnel

The following individuals received financial support from this grant:

<u>Name</u>	<u>Status</u>	<u>Comments</u>
J. W. Barlow	Faculty	Summer Support
E. Woo	Ph.D. Student	Degree Granted, June, 1984
A. Fernandes	Ph.D. Student	Continuing
M. Fowler	Ph.D. Student	Continuing
S. Murff	M.S. Student	Degree Granted, August, 1983
W. Preston	M.S. Student	Degree Granted, August, 1983
J. Chiou	Ph.D. Student	Continuing, Degree Expected, Dec. 1984.
P. Tucker	Ph.D. Student	Continuing
M. Schwarz	Ph.D. Student	Continuing

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